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**CERAMIC FUEL CELLS LIMITED**

**A U S T R A L I A**

**Patents Act 1990**

**PROVISIONAL SPECIFICATION**

for the invention entitled:

**"AIR-SIDE SOLID OXIDE FUEL CELL COMPONENTS"**

The invention is described in the following statement:

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## AIR-SIDE SOLID OXIDE FUEL CELL COMPONENTS

The present invention relates to solid oxide fuel cells and is particularly concerned with components for solid oxide fuel cells systems which are adapted to be exposed to a temperature in excess of 750°C and to an oxidising atmosphere. Such components include gas separators between adjacent fuel cells, and heat exchangers.

The purpose of a gas separator in planar fuel cell assemblies is to keep the oxygen containing gas supplied to the cathode side of one fuel cell away from the fuel gas supplied to the anode side of an adjacent fuel cell and to conduct heat generated in the fuel cells away from the fuel cells. The gas separator may also conduct electricity generated in the fuel cells away from the fuel cells, but this function may alternatively be performed by a separate member between each fuel cell and the gas separator.

Sophisticated ceramics for use in fuel cell gas separators have been developed which are electrically conductive, but these suffer from a relatively high fragility, low thermal conductivity and particularly high cost. Special alloys have also been developed, but it has proved difficult to avoid the various materials of the fuel cell assembly and the interfaces between them degrading or changing substantially through the life of the fuel cell, particularly insofar as their electrical conductivity is concerned, because of the tendency of different materials to interact at the high temperatures which are required for efficient operation of a solid oxide fuel cell. For example, most metallic gas separators contain substantial quantities of the element chromium which is used to impart oxidation resistance to the metal as well as other properties.

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It has been found that where chromium is present in more than minute quantities it may combine with oxygen or oxygen plus moisture to form highly volatile oxide or oxyhydroxide gases under conditions which are typical of those experienced in operating solid oxide fuel cells. These volatile gases are attracted to the cathode-electrolyte interface where they may react to form compounds which are deleterious to the efficiency of the fuel

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cell. If these chromium reactions are not eliminated or substantially inhibited, the performance of the fuel cell deteriorates with time to the point where the fuel cell is no longer effective. Several of these alloys and one proposal for alleviating this problem are described in our patent application WO96/28855 in which a chromium-containing gas separator is  
5 provided with an oxide surface layer which reacts with the chromium to form a spinel layer between the substrate and the oxide surface layer and thereby tie in the chromium. However, these specialist alloys remain too expensive for substantial use in fuel cell assemblies.

Special heat resistant steels have also been developed which are stable at high  
10 temperature in fuel cell atmospheres. The significant feature of all heat resistant steels is the oxide layer, particularly its type and nature, which is formed when the steel is exposed to mildly and strongly oxidising conditions at elevated temperatures. Heat resisting steels form tight, adherent, dense oxide layers which prevent further oxidation of the underlying metal. These  
oxide layers are composed of chromium, aluminium or silicon oxides or some combination of  
15 these. These oxide layers are very effective in providing a built-in resistance to degradation due to high temperature oxidation.

However, while this feature is used to advantage in many applications, the presence of this oxide layer has until recently been considered to inhibit the use of these steels in key  
20 components of solid oxide fuel cells. The oxides, especially those of silicon and aluminium, are electrically insulating at all temperatures, and this is a major problem for those components in a fuel cell which must act as electrical current collectors. Of all the heat resisting steels available, those based on the iron-chromium binary systems are the best in this regard, but they too have severe limitations. In particular, they generally contain more than 12 wt% chromium to  
25 provide the desired oxidation resistance, leading to the problems described above. At levels of less than 12 wt% Cr, tight, adherent, dense chromium oxide layers do not form on the iron-chromium alloys and the alloys are unsuitable for use in oxidising atmosphere at elevated temperatures. At chromium contents of 12 wt% or more, special coatings or treatments are again required to prevent the chromium-based gases escaping from a gas separator formed of  
30 the alloy.

One approach to alleviating these disadvantages of heat resistant steel gas separators is described in our patent application PCT/AU98/00956. However, this and most other heat resistant steels are specialist materials containing substantial levels of Cr plus other compositional controls which means that their cost will remain high.

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It is an object of the present invention to provide a component for a solid oxide fuel cell system formed of a heat resistant steel which is adapted to be exposed to a temperature in excess of 750°C and to an oxidising atmosphere, but in which the aforementioned disadvantages may be alleviated.

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According to the present invention there is provided a solid oxide fuel cell system component which is adapted to be exposed to an oxidising atmosphere in the fuel cell system and which is formed of a heat resistant alloy having a composition, in wt%, of:

	Al		5.0 - 10.0
15	Si		0.1 - 3.8
	Mn	≤	0.5
	Cu	≤	0.23
	Ni	≤	0.61
	C	≤	0.02
20	P	≤	0.04
	S	≤	0.04
	Cr	≤	5.0

Residue Fe, excluding incidental impurities.

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Further according to the present invention, there is provided a solid oxide fuel cell system in which one or more components adapted to be exposed to a temperature in excess of 750°C and an oxidising atmosphere are formed of a heat resistant alloy having a composition as defined in the immediately preceding paragraph.

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The component may be in the form of a manifold, base plate, current collector strap, ducting or, for example, a heat exchanger or heat exchanger plate used in a solid oxide fuel cell system, but preferably the component is a gas separator disposed or adapted to be disposed between adjacent fuel cells.

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An advantage of solid oxide fuel cell system components in accordance with the invention is that they are capable of forming a stable alumina oxide layer on the surface when exposed to oxidising atmosphere at elevated temperature. The component preferably does not contain any chromium, but levels up to about 5 wt% have been found to not interfere with the formation of an alumina layer which can then prevent the escape of chromium vapour. The formation of the alumina layer may be performed by heating in an oxidising atmosphere at a temperature of at least 950°C, preferably no more than 1200°C and more preferably in the range 1000 - 1100°C. The length of the heat treatment is dependent upon the elevated temperature. For example, at temperatures in the range of 1200°C, a sufficient thickness of alumina may be formed on the component surface in 1 hour or less. At the lowest temperature of 950°C, a sufficient thickness of alumina may take 10 - 20 hours or more to form. The alumina layer preferably has a thickness as small as 1 - 3  $\mu\text{m}$ , but greater thicknesses up to 5 or even 10 microns may be acceptable.

20 A minimum level of 5 wt% Al is necessary in the components in order to form the alumina layer when subjected to the heat treatment. A maximum of about 10 wt% Al is provided in order to ensure that the alloy of the component remains within the cold workability limit for Fe - Si - Al alloys. The maximum may be varied by other alloying elements which are acceptable in a fuel cell component exposed to oxidising atmosphere at elevated temperature, but the preferred maximum is about 8.5 wt% since no advantage has been recognised in adding more.

The silicon content of the alloy is also restricted by the cold workability considerations and by other steel-making considerations. With increasing aluminium content, the silicon content may be decreased in order to ensure the alloy remains within the cold workability

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limit, and preferably the Si content is no more than about 1.5 wt%. At higher levels, and possibly even at levels above about 1 wt% Si, processing difficulties may be encountered when large volumes of the alloy are made because of the formation of fayalite at elevated temperature. The presence of Si in the Fe-Al alloy assists the fluidity of the aluminium at high levels of the metal when the components are being melted. A minimum 0.1 wt% Si also alleviates the formation of iron oxide nodules should the alumina surface layer be damaged.

Preferably any manganese present is at levels of less than 0.05 wt% since alloys containing more Mn than this may be difficult to roll.

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Manganese and the other non-Fe-Al-Si elements may be present as tramp elements, and advantageously the alloy composition may be produced from selected scrap metal, including, but not restricted to, cast and other forms of aluminium, aluminium-silicon alloys, all other aluminium alloy scrap, recycled steel and aluminium cans, Fe-Si transformer core scrap and plain steel, particularly low alloy plain carbon steels. In addition, ferro-silicon and ferro-aluminium alloys of the type used for modifying steel compositions during production are suitable source materials for the Fe-Al-Si alloy.

The preferred alloy composition is, in wt%:

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Al  $6.0 \pm 1.0$

Si  $1.0 \pm 0.5$

C  $0.005 - 0.02$

P  $\leq 0.04$

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S  $\leq 0.04$

Cr  $\leq 0.10$

(Al + Si) = 6.5 - 7.5

Residue Fe, excluding incidental impurities.

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The alloys may be prepared by, for example, argon arc melting or any other standard steel making process, such as open hearth, BOS, etc.

The most preferred alloy composition having no Cr conveys particular benefits for gas  
5 separators of solid oxide fuel cell assemblies and other components in contact with the inlet air stream to the cells since any breakdown, damage or loss of the  $\text{Al}_2\text{O}_3$  layer, for whatever reason, can not lead to Cr egress as it can with all Cr containing steels/other heat resisting steels and alloys.

10 A component in the form of a gas separator in accordance with the present invention may have gas channels formed on opposed sides, for example as described in our aforementioned patent application WO 96/28855. However, preferably, the gas flow passages are formed in or provided by a mesh or other structure provided between the respective side  
15 of the gas separator and the adjacent electrode, for example as described in our patent application WO 98/57384.

Most preferably, a gas separator in accordance with the invention would be used with a separate electrical conductor between the gas separator and each electrode. One proposal for separate electrical conductors on respective sides of a gas separator is disclosed in our  
20 patent application WO 99/13522.

#### Examples:

25 The Fe-Al-Si alloy system was investigated to find a suitable alumina-forming alloy for particular application as a non-current collecting gas separator. Initial work was conducted on a total of 12 alloy compositions, including one quaternary alloy containing chromium. Alloys were prepared by argon arc melting and their oxidation behaviour and mechanical properties were assessed. Compositions are listed in Table I below.

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Table 1. Alloy compositions by atomic %

Alloy No	Nominal Composition, at. %	Alloy No	Nominal Composition, at. %
1	Fe-10.5Al-2Si	7	Fe-11.5Al-2Si
2	Fe-4Al-5Si	8	Fe-1Al-7Si
3	Fe-20Al-1 Si-5Cr	9	Fe-12Al-1.25Si
4	Fe-5Al-4.5Si	10	Fe-13 Al-1Si
5	Fe-20Al-1Si	11	Fe-14Al-0.75Si
6	Fe-15Al-0.5Si	12	Fe-11Al-1.85Si

10 In the Fe-Al-Si ternary system atomic % equates to approximately 2 x weight %.

Most of the alloys in Table 1 (Alloy Nos 1, 2, 4, and 6-12) fall within the  $\alpha$ -Fe phase field (corresponding to the cold-working range) of the ternary Fe-Al-Si system, as shown in the Fe-Al-Si ternary phase diagram in Figure 1. Alloy 5 and alloy 3, based on the ductile Fe-20Al  
15 (at.%), fall just outside this range but were still found to be workable.

A second series of alloys 15 to 19 was prepared with selected additions to determine the effect of minor elements, commonly present in stainless steel scrap, on rolling and oxidation behaviour. Compositions are listed in Table 2.

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Table 2. Alloy Compositions by atomic %

Alloy Number	Composition, at. %
15	Fe-11.5Al-2Si-1Mn
16	Fe-11.5Al-2Si-0.2Cu
17	Fe-11.5Al-2Si-0.55Ni
18	Fe-11.5Al-2Si-0.2Cu-0.5Ni
19	Fe-11.5Al-2Si-1Mn-0.2Cu-0.5Ni

All alloys 1 - 12 and 15-19 were successfully hot rolled at 900°C. Small ingot samples  
30 were rolled to approximately 1mm thickness, using ~30% roll-reductions. All rolled alloys were

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posted-annealed at 900°C for 1 hour and all were successfully cold rolled, using ~35% roll-reductions, except for Alloy No. 3.

#### Oxidation Behaviour

5           Oxidation tests on alloys 1- 12 and 15-19 were conducted at 900°C for 100 hours in static air and the oxidised samples were examined by XRD and SEM. All of the alloys produced thin, adherent alumina surface scales, except for Alloy Nos. 2 - 4 and 8. In the case of alloys 2 to 4, nodular iron oxides or multi-layered scales were formed and some spalling was observed. Continued growth of these iron oxides over longer exposure times resulted in the catastrophic  
10 failure of the scales. In the case of alloy 8 no alumina surface scale was formed and the alloy would produce processing difficulties in larger volumes due to the formation of fayalite. No silicon oxides were detected in any of the samples, except sample 8, by XRD, but silicon was detected in the alumina scales using EDAX.

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15           This shows that Fe-Al-Si alloys having a composition range in accordance with the invention are capable of forming thin, adherent alumina oxidation resistant surface layers. This permits the alloys to be used in non-electrically conductive, heat resistant components on the oxygen-containing gas side of a fuel cell assembly, particularly in gas separators. The alloys in accordance with the invention have thermal conductivities suitable to enable them to readily  
20 transfer heat away from the adjacent fuel cell or cells.

          Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within  
25 its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps, features, compositions and components.

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Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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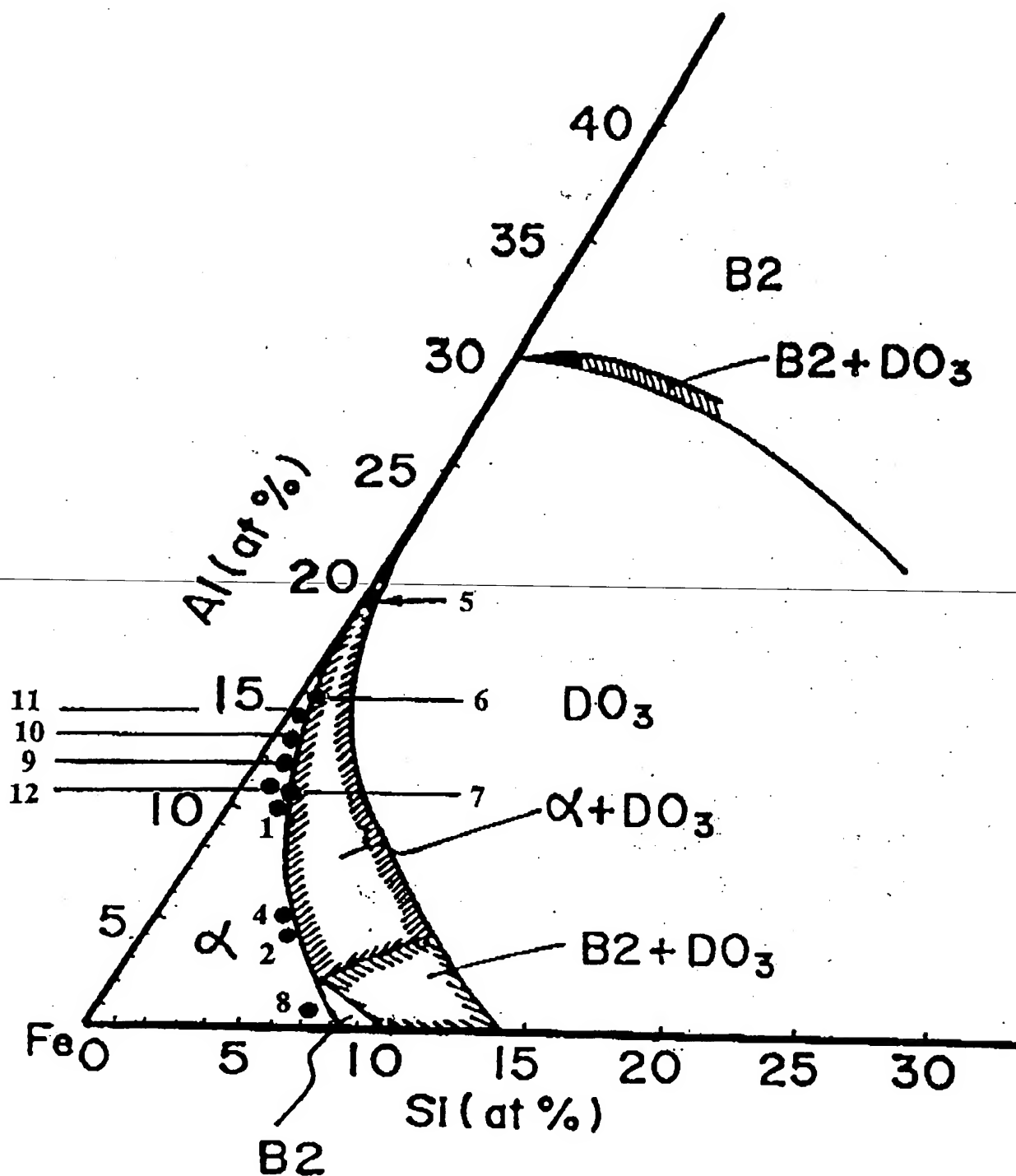


Figure Fe-Al-Si Ternary phase diagram at 455°C, showing alloy compositions.